

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-356384

(43)Date of publication of application : 13.12.2002

(51)Int.Cl.

C04B 38/08
B01D 39/20
C04B 35/565
C04B 35/571
C04B 38/06
F01N 3/02

(21)Application number : 2001-166780

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(22)Date of filing : 01.06.2001

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(54) SILICON CARBIDE BASED POROUS COMPACT AND METHOD OF MANUFACTURING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a silicon carbide based porous compact and a method of manufacturing the same which is containing a silicon carbide grain and a silicon nitride grain, excellent in heat resistance, corrosion resistance, chemical resistance, strength, heat shock resistance, and preferable for collecting and eliminating particulates.

SOLUTION: The method of manufacturing the silicon carbide based porous compact is characterized in that a compact formed of 70-98 mass% mixed powder composed of 70-95 mass% silicon carbide grain of 10-100 μm mean grain diameter, 5-30 mass % metallic silicon grain of 1-50 μm mean grain diameter, and 2-30 mass % pore generating agent, is heat treated in a nitrogen atmosphere so as to nitride the metallic silicon grain.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開2002-356384

(P2002-356384A)

(43) 公開日 平成14年12月13日 (2002. 12. 13)

(51) Int.Cl. ⁷	識別記号	F I	テームト [*] (参考)
C 0 4 B 38/08		C 0 4 B 38/08	D 3 G 0 9 0
B 0 1 D 39/20		B 0 1 D 39/20	D 4 D 0 1 9
C 0 4 B 35/565		C 0 4 B 38/06	E 4 G 0 0 1
35/571		F 0 1 N 3/02	3 0 1 D 4 G 0 1 9
38/06		C 0 4 B 35/56	1 0 1 M
審査請求 未請求 請求項の数 9 O L (全 5 頁) 最終頁に続く			

(21) 出願番号 特願2001-166780(P2001-166780)

(22) 出願日 平成13年6月1日 (2001. 6. 1)

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(54) 【発明の名称】 炭化ケイ素質多孔体およびその製造方法

(57) 【要約】

【課題】耐熱性、耐食性、耐薬品性、強度、耐熱衝撃性に優れた、パティキュレートの捕集・除去に好適で、炭化ケイ素粒子と窒化ケイ素粒子とを含む炭化ケイ素質多孔体およびその製造方法を提供する。

【解決手段】平均粒子直径10～100 μ mの炭化ケイ素粒子70～95質量%と平均粒子直径1～50 μ mの金属ケイ素粒子5～30質量部とからなる混合粉末70～98質量%と気孔形成剤2～30質量%とを含む成形体を、窒素雰囲気中で熱処理し前記金属ケイ素粒子を窒化することを特徴とする。

【特許請求の範囲】

【請求項 1】平均粒子直径 10～100 μm の炭化ケイ素粒子 70～95 質量%と平均粒子直径 1～50 μm の金属ケイ素粒子 5～30 質量%とからなる混合粉末 70～98 質量%と、気孔形成剤 2～30 質量%とを含む成形体を、窒素雰囲気中で熱処理し前記金属ケイ素粒子を窒化することを特徴とする炭化ケイ素質多孔体の製造方法。

【請求項 2】前記気孔形成剤がセラミックス粒子および／または熱分解性の有機高分子粒子である請求項 1 記載の炭化ケイ素質多孔体の製造方法。

【請求項 3】前記セラミックス粒子が酸化物セラミックス中空粒子である請求項 2 記載の炭化ケイ素質多孔体の製造方法。

【請求項 4】前記酸化物セラミックス中空粒子が、Al、Si、Ca、Sr、Y、Yb、Ba および Mg からなる群から選ばれる 1 種以上の金属の酸化物を主成分とする請求項 3 記載の炭化ケイ素質多孔体の製造方法。

【請求項 5】前記気孔形成剤の平均粒子直径が 5～100 μm である請求項 2、3 または 4 記載の炭化ケイ素質多孔体の製造方法。

【請求項 6】請求項 1～5 のいずれか記載の炭化ケイ素質多孔体の製造方法で製造される炭化ケイ素質多孔体。

【請求項 7】前記炭化ケイ素質多孔体の平均細孔直径が 5～20 μm である請求項 6 記載の炭化ケイ素質多孔体。

【請求項 8】前記炭化ケイ素質多孔体の気孔率が 30～80% である請求項 6 または 7 記載の炭化ケイ素質多孔体。

【請求項 9】前記炭化ケイ素質多孔体が実質的に炭化ケイ素粒子と窒化ケイ素粒子とからなる請求項 6、7 または 8 記載の炭化ケイ素質多孔体。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、高温排気ガス中に含まれる粉塵等を除去するために好適な炭化ケイ素質多孔体の製造法に関する。

【0002】

【従来の技術】炭化ケイ素は、耐熱性、耐食性、耐薬品性、強度等に優れた特性を有しており、高温や腐食性環境下での集塵または脱塵用フィルタとして期待されている。

【0003】しかし、炭化ケイ素は比較的熱膨張率が高いことから耐熱衝撃性は充分ではなく、特にディーゼルエンジンからの排気ガス中に含まれるディーゼルバティキュレート（以下、単にバティキュレートと略す）を除去するバティキュレートフィルタのような耐熱衝撃性を必要とするようなフィルタではその点の改善が求められている。

【0004】これを解決するため、特開 2000-35

1679 には、炭化ケイ素を熱膨張率の低い酸化物セラミックスにより結合した炭化ケイ素質多孔体の製造方法が提案されている。しかし、この方法では、結合部分が酸化物セラミックスであるため酸やアルカリなどに腐食を受けやすく耐食性に劣るという欠点があった。

【0005】同様に、特開平 5-9074 には、炭化ケイ素と窒化ケイ素の複合体として、炭化ケイ素、窒化ケイ素および遊離炭素からなる気孔率が 5% 以下の緻密なセラミックス複合焼結体が提案されている。しかし、気孔率が 5% 以下であることから明かなようにフィルタとしては緻密過ぎて使用できない。また、加圧窒素雰囲気下で焼結するため専用の設備が必要となり、生産性、原価などの点でも問題がある。

【0006】また、特開平 9-227244 には、炭化ケイ素ウイスキーの多孔質層と窒化ケイ素の緻密質層を積層したセラミックス複合体が提案されているが、高温ガスタービン用部材、自動車用エンジン部材および超高速航空機用部材等として有用であるもののフィルタとしては適さない。

【0007】いずれにせよ、耐熱性、耐食性、耐薬品性、強度以外に耐熱衝撃性にも優れたフィルタであって、炭化ケイ素と窒化ケイ素とを含むフィルタについては提案されていない。

【0008】

【発明が解決しようとする課題】本発明は、耐熱性、耐食性、耐薬品性、強度、耐熱衝撃性に優れた、バティキュレートの捕集・除去に好適で、炭化ケイ素粒子と窒化ケイ素粒子とを含む炭化ケイ素質多孔体およびその製造方法の提供を目的とする。

【0009】

【課題を解決するための手段】本発明は、平均粒子直径 10～100 μm の炭化ケイ素粒子 70～95 質量%と平均粒子直径 1～50 μm の金属ケイ素粒子 5～30 質量%とからなる混合粉末 70～98 質量%と、気孔形成剤 2～30 質量%とを含む成形体を、窒素雰囲気中で熱処理し前記金属ケイ素粒子を窒化することを特徴とする炭化ケイ素質多孔体の製造方法である。

【0010】

【発明の実施の形態】本発明の炭化ケイ素質多孔体の製造法（以下、本製造法という）では、平均粒子直径 10～100 μm の炭化ケイ素粒子 70～95 質量%と平均粒子直径 1～50 μm の金属ケイ素粒子 5～30 質量%とからなる混合粉末 70～98 質量%と、気孔形成剤 2～30 質量%とを含む成形体を使用する。

【0011】気孔形成剤としては、熱処理時に分解などして飛散し、気孔を形成するものであれば有機物、無機物のいずれも好適に使用されるが、セラミックス粒子、熱分解性の有機高分子粒子であると好ましい。気孔形成剤がセラミックス粒子であると焼結助剤のような働きを兼ねられるため好ましく、一方、熱分解性の有機高分子

粒子であると、熱処理過程で分解、飛散し、焼結体内に残留物を残さず得られる炭化ケイ素質多孔体の特性を損なわないため好ましい。

【0012】このような気孔形成剤に用いるセラミックス粒子としては、酸化物セラミックス、窒化物セラミックス、炭化物セラミックス、珪化物セラミックス、などが挙げられる。なかでも窒化により生成する窒化ケイ素粒子に対して焼結助剤のような効果があることから酸化物セラミックスが好ましく、特に中空形状を有する酸化物セラミックス中空粒子（以下、中空粒子という）であると、少ない添加量で気孔形成できるためさらに好ましい。

【0013】中空粒子としては、熱処理時に気孔を形成し、しかも熱処理過程で生成する窒化ケイ素粒子に対して焼結助剤的な働きをするものであればいずれも好適に使用される。中空粒子は、Al、Si、Ca、Sr、Y、Yb、BaおよびMgからなる群から選ばれる1種以上の金属の酸化物を主成分とすると焼結助剤的な効果が高いため好ましい。中空粒子は、中空であれば外皮に相当する部分が緻密質でもよいし、多孔質でもよい。また、中空粒子は、外形が球状粒子であると入手しやすいので好ましいが、球状粒子以外の粒子でも中空であればよい。

【0014】中空粒子の平均粒子直径が30～100 μ mであると、得られる多孔体の気孔率が大きく、しかも強度も確保されるため好ましい。中空粒子の平均粒子直径が30 μ m未満であると、細孔直径が小さくなりすぎる上に気孔形成への寄与が低下する。一方、平均粒子直径が100 μ mを超えると気孔径が大きくなりすぎ、得られる多孔体の強度が不充分であるため好ましくない。

【0015】また、気孔付与剤として用いられる有機高分子粒子としては、ポリビニルアルコール、アクリル樹脂、酢酸ビニル樹脂、セルロースなどの粒子がある。昇温中に、気孔形成剤として添加した有機高分子粒子が、熱処理の昇温段階で十分に熱分解されずに炭素として残留すると、その後の熱処理過程で金属ケイ素粒子と反応して窒化ケイ素ではなく炭化ケイ素が生成されてしまい、耐熱衝撃性の向上の点で好ましくない。その点、アクリル樹脂粒子を気孔形成剤とすると熱分解しやすく、炭素として残留する量が少ないため好ましい。

【0016】気孔形成剤の含有量としては、成形体中2～30質量%である。含有量が2質量%未満では、多孔体として気孔の割合が充分でなく、一方、含有量が30質量%を超えると多孔体の気孔率が大きくなるものの、充分な強度が得られない。気孔形成剤の含有量が成形体中5～25質量%であると、多孔体の強度と気孔率の両方を高くできるため好ましい。

【0017】さらに、気孔形成剤が球形であると形成される気孔も球状となり気孔率を高くしても強度の低下を抑制できるので特に好ましい。

【0018】また気孔形成剤の平均粒子直径が5～100 μ mであると好適である。気孔形成剤の平均粒子直径が5 μ m未満であると熱処理後得られる炭化ケイ素質多孔体の平均細孔直径が5 μ m以下となり好ましくなく、一方、100 μ mを超えると熱処理後得られる炭化ケイ素質多孔体の平均細孔直径が40 μ m以上となって除塵等のフィルタとして好ましくない。

【0019】本製造法に用いる金属ケイ素粒子は、平均粒子直径が1～50 μ mである。金属ケイ素粒子の平均粒子直径が1 μ m未満であると、成形体作成中などに外気の酸素や水分を吸着する量が増大し、焼結が進行しにくいというに、熱処理したときに金属ケイ素粒子が窒化される前に酸化されて生成する二酸化ケイ素の量が大きくなりすぎる。また、金属ケイ素粒子の平均粒子直径が50 μ mを超えると、熱処理後にも焼結体内部に窒化されない金属ケイ素粒子が残留し最終的な多孔体としての特性が低下する。なお、金属ケイ素粒子の純度としては目的、用途に応じ適宜選択される。

【0020】本製造法において、気孔形成剤と金属ケイ素粒子とを含む成形体を作成する方法としては、プレス成形、押出成形、鋳造成形などの通常のセラミックス成形法が適宜採用される。なお、成形に際して、気孔形成剤とは別に有機バインダを加えてもよい。このような有機バインダとしては、ポリビニルアルコールまたはその変成物、でんぶんまたはその変成物、カルボキシルメチルセルロース、ヒドロキシルメチルセルロース、ポリビニルピロリドン、アクリル樹脂またはアクリル系共重合体、酢酸ビニル樹脂または酢酸ビニル系共重合体、等の有機物を使用できる。このような有機バインダの添加量として前記混合粉末100質量部に対して1～10質量部とすると好ましい。なお、気孔形成剤が成形体のバインダの働きをかねてもよい。

【0021】前記成形体を熱処理する条件としては、窒素雰囲気下で1100～1800℃で2～24時間保持することが好ましい。温度範囲が1100℃未満であると金属ケイ素粒子の窒化が進まないため好ましくなく、1800℃を超えると生成した窒化ケイ素粒子が分解するので好ましくない。温度保持時間が2時間未満であると粒子同士の結合が充分に進行しないため好ましくなく、一方、24時間を超えると特に、高温では窒化ケイ素が分解しやすくなり好ましくない。

【0022】熱処理時の昇温速度は、成形体の大きさ、形状等により適宜選択されるが、50～600℃/hであると窒化率、気孔直径の点で好ましい。ここで窒素雰囲気とは、実質的に窒素のみを含み酸素を含まない雰囲気というが、他の不活性気体を含んでいてもよい。窒素分圧は50kPa以上が好ましい。

【0023】本製造法で得られる炭化ケイ素質多孔体（以下、単に本炭化ケイ素質多孔体と略す）の気孔率は、30～80%であると好適である。気孔率が30%

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未満であるとフィルタとして用いる場合、圧力損失が大きくなるため多孔体として好ましくない。また気孔率が80%を超えると強度が低くなるため多孔体として好ましくない。

【0024】本炭化ケイ素質多孔体の平均細孔直径は、5~20 μ mであると好ましい。平均細孔直径が5 μ m未満であると多孔体使用時の圧力損失が大きくなり好ましくない。平均細孔直径が20 μ mを超えるとディーゼルバディキュレートのような排気微粒子の捕捉除去がしにくくなるため好ましくない。

【0025】本炭化ケイ素質多孔体の組織は、炭化ケイ素粒子を窒化ケイ素および金属ケイ素粒子で結合した微細構造を有するため耐熱衝撃性に優れる特徴がある。

【0026】

【実施例】以下に実施例(例1、例4、例5)と比較例(例2、例3、例6)を示す。

【0027】[例1] 平均粒子直径50 μ mの炭化ケイ素粒子80質量%と平均粒子直径10 μ mの金属ケイ素粒子20質量%との混合粉末75質量部に、平均粒子直径20 μ mのアクリル樹脂系の球状粒子を25質量部添加し、さらにエタノールを分散媒として添加し、ボールミル法によって30分間湿式混合して、最後に乾燥した。得られた成形体用粉末を40mm \times 60mmのプレス金型に充填し、成形圧20MPaで一軸加圧成形を行った。成形後、電気炉中、窒素雰囲気下で、室温~1000℃まで400℃/hで昇温し、1500℃まで60℃/hで昇温し1500℃で10時間保持して熱処理し多孔体を得た。

【0028】[例2] 例1において熱処理条件が真空中で、室温~1000℃まで400℃/hで昇温し、1350℃まで300℃/hで昇温し1350℃で5時間保持して熱処理する以外は例1と同様にして多孔体を得た。

【0029】[例3] 例1において、金属ケイ素の代わりに平均粒子直径が10 μ mのリチウムアルミニウムシリケートを用い熱処理条件を、アルゴン中で、室温~1000℃まで400℃/hで昇温し、1000~1300℃まで300℃/hで昇温し1300℃で5時間保持して熱処理する以外は例1と同様にして多孔体を得た。

【0030】[例4] 例1において熱処理条件が窒素雰囲気中で、室温~1000℃まで400℃/hで昇温し、1400℃まで400℃/hで昇温し1400℃で時間保持して熱処理する、以外は例1と同様にして多孔体を得た。

【0031】[例5] 平均粒子直径75 μ mの炭化ケイ素粒子70質量%と平均粒子直径10 μ mの金属ケイ素粒子30質量%とからなる混合粉末85質量部に、平均粒子直径40 μ mのアルミナ-シリカ系のセラミックス中空球状粒子15質量部を添加し、さらにエタノールを分散媒として添加し、ボールミル法によって30分間湿式混合して、最後に乾燥した。

【0032】得られた成形体用粉末を40mm \times 60mmのプレス金型に充填し、成形圧20MPaで一軸加圧成形を行った。成形後、電気炉中、窒素雰囲気下で、室温~1000℃まで400℃/hで昇温し、1700℃まで60℃/hで昇温し1700℃で5時間保持して熱処理し多孔体を得た。

【0033】[例6] 例1において金属ケイ素粒子を使用しない以外は例1と同様にして多孔体を得た。

【0034】[評価方法] 各々の多孔体について気孔率、平均細孔直径、熱膨張率、結晶相、室温曲げ強度、高温曲げ強度、耐酸性、耐熱衝撃性を測定、評価した。

10 気孔率(%) : アルキメデス法で測定。
平均細孔直径d(μ m) : 水銀ポロシメータ(ユアサアイオニクス社製、商品名: AUTOSCAN-33)で測定。

熱膨張係数 α ($\times 10^{-6}/^{\circ}\text{C}$) : 線熱膨張率測定装置(リガク社製、商品名: TAS100)を用い、室温~1000℃の範囲で測定。

結晶相 : X線回折により同定。SC、SN、S、LASはそれぞれ炭化ケイ素、窒化ケイ素、金属ケイ素、リチウムアルミニウムシリケートの結晶相を示す。強度 σ (MPa) : 試料より4mm \times 3mm \times 40mmサイズの曲げ試験片を切り出し、室温で3点曲げ強度(スパン30mm)を測定。荷重印加速度は、0.5mm/分とした。耐食性(%) : 80℃で1モル%の硫酸水溶液に試料を50時間浸漬し、浸漬前後の3点曲げ強度をそれぞれ測定し、浸漬前の試料の曲げ強度からの強度低下率を算出して評価した。強度低下率が低い程、耐食性が良好である。耐熱衝撃性 ΔT : 高温に保持した試験片を氷水(約3℃)に投入して急冷させ、急冷後の試験片の曲げ強度を測定し、曲げ強度の値が急冷前の試験片の曲げ強度の値より低下したときの保持温度と氷水との温度差を耐熱衝撃温度差として評価した。温度差は50℃間隔で評価した。なお、曲げ強度の試験片サイズ、試験方法は前述の強度測定に準ずる。評価結果を表1に示す。

【0035】

【表1】

7	8					
	例1	例2	例3	例4	例5	例6
気孔率	35	40	30	37	40	50
d	15	17	16	12	15	20
結晶相	SC、SN	SC、S	SC、LAS	SC、SN、S	SC、SN	SC
α	3.6	4.1	3.0	3.8	3.2	4.6
σ	42	30	31	33	53	5
ΔT	500	300	400	400	500	300
耐食性	15	40	50	30	10	10

【0036】窒化ケイ素を含む炭化ケイ素質多孔体であると、窒化ケイ素を含まない炭化ケイ素質多孔体に比べて、耐熱衝撃性、耐食性が向上していることがわかる。

【0037】

【発明の効果】従来の窒化ケイ素粒子を含まない炭化ケイ素質多孔体に比べて、金属ケイ素粒子を窒化させた窒化*

10*ケイ素粒子を含む本炭化ケイ素質多孔体は、耐熱衝撃性、耐熱性、耐食性、耐薬品性、強度等に優れた特性を有する。

【0038】したがって、温度変化の激しい気体を取り扱うフィルタとして好適であり、特にバティキュレートフィルタとして優れた性能を示す。

フロントページの続き

(51)Int.Cl.⁷

F01N 3/02

識別記号

301

F I

C04B 35/56

テーマコード(参考)

101S

Fターム(参考) 3G090 AA02

4D019 AA01 BA05 BB06 BC12 BD01

4G001 BA03 BA04 BA05 BA06 BA07

BA08 BA09 BA22 BA62 BB03

BB04 BB05 BB06 BB07 BB08

BB09 BB22 BB32 BC13 BC54

BD01 BD04 BD13 BD37 BE31

BE33 BE34

4G019 LA07 LB01 LD02

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the nature porous body of silicon carbide characterized by heat-treating the Plastic solid containing the mixed powder 70 which consists of the silicon carbide particle 70 with a mean particle diameter of 10-100 micrometers - 95 mass %, and five to metal silicon particle 30 with a mean particle diameter of 1-50 micrometers mass % - 98 mass %, and the pore formation agent 2 - 30 mass % in nitrogen-gas-atmosphere mind, and nitriding said metal silicon particle.

[Claim 2] The manufacture approach of the nature porous body of silicon carbide according to claim 1 that said pore formation agents are a ceramic particle and/or the organic macromolecule particle of pyrolysis nature.

[Claim 3] The manufacture approach of the nature porous body of silicon carbide according to claim 2 that said ceramic particle is an oxide-ceramics empty capsid.

[Claim 4] The manufacture approach of the nature porous body of silicon carbide according to claim 3 that said oxide-ceramics empty capsid uses as a principal component the oxide of one or more sorts of metals chosen from the group which consists of aluminum, Si, calcium, Sr, Y, Yb, Ba, and Mg.

[Claim 5] The manufacture approach of the nature porous body of silicon carbide according to claim 2, 3, or 4 that the mean particle diameter of said pore formation agent is 5-100 micrometers.

[Claim 6] Claims 1-5 are the nature porous bodies of silicon carbide manufactured by the manufacture approach of the nature porous body of silicon carbide a publication either.

[Claim 7] The nature porous body of silicon carbide according to claim 6 whose average pore diameter of said nature porous body of silicon carbide is 5-20 micrometers.

[Claim 8] The nature porous body of silicon carbide according to claim 6 or 7 whose porosity of said nature porous body of silicon carbide is 30 - 80%.

[Claim 9] The nature porous body of silicon carbide according to claim 6, 7, or 8 which said nature porous body of silicon carbide turns into from a silicon carbide particle and a nitriding cay elementary particle substantially.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacturing method of the suitable nature porous body of silicon carbide, in order to remove the dust contained in elevated-temperature exhaust gas.

[0002]

[Description of the Prior Art] Silicon carbide has the property excellent in thermal resistance, corrosion resistance, chemical resistance, reinforcement, etc., and is expected as a filter for dust collection or dust removals under an elevated temperature or a corrosive environment.

[0003] However, since coefficient of thermal expansion of silicon carbide is comparatively high, thermal shock resistance is not enough and the improvement of the point is called for with a filter which needs thermal shock resistance like the particulate filter from which the diesel particulate (it only abbreviates to a particulate hereafter) especially contained in the exhaust gas from a diesel power plant is removed.

[0004] In order to solve this, the manufacture approach of the nature porous body of silicon carbide which combined silicon carbide with oxide ceramics with a low coefficient of thermal expansion is proposed by JP,2000-351679,A. However, by this approach, since the amount of bond parts were oxide ceramics, there was a fault that that it is easy to receive corrosion in an acid, alkali, etc. it was inferior to corrosion resistance.

[0005] Similarly, 5% or less of substantia compacta ceramic compound sintered compact is proposed for the porosity which consists of silicon carbide, silicon nitride, and free carbon by JP,5-9074,A as complex of silicon carbide and silicon nitride. However, as a filter, it is too precise to use it so that clearly from porosity being 5% or less. Moreover, in order to sinter under pressurization nitrogen-gas-atmosphere mind, a facility of dedication is needed, and there is a problem also in respect of productivity, the cost price, etc.

[0006] Moreover, although the ceramic complex which carried out the laminating of the porous layer of a silicon carbide whisker and the substantia-compacta layer of silicon nitride is proposed by JP,9-227244,A, and it is useful as the member for elevated-temperature gas turbines, a car motor member, a member for ultra high-speed aircrafts, etc., as a filter, it is not suitable.

[0007] Anyway, it is the filter which was excellent also in thermal shock resistance in addition to thermal resistance, corrosion resistance, chemical resistance, and reinforcement, and is not proposed about the filter containing silicon carbide and silicon nitride.

[0008]

[Problem(s) to be Solved by the Invention] It is suitable for particulate uptake and removal excellent in thermal resistance, corrosion resistance, chemical resistance, reinforcement, and thermal shock resistance, and this invention aims at offer of the nature porous body of silicon carbide containing a silicon carbide particle and a nitriding cay elementary particle, and its manufacture approach.

[0009]

[Means for Solving the Problem] This invention is the manufacture approach of the nature porous body of silicon carbide characterized by heat-treating the Plastic solid containing the mixed powder 70 which consists of the silicon carbide particle 70 with a mean particle diameter of 10-100 micrometers - 95 mass %, and five to metal silicon particle 30 with a mean particle diameter of 1-50

micrometers mass % - 98 mass %, and the pore formation agent 2 - 30 mass % in nitrogen-gas-atmosphere mind, and nitriding said metal silicon particle.

[0010]

[Embodiment of the Invention] In the manufacturing method (henceforth this manufacturing method) of the nature porous body of silicon carbide of this invention, the Plastic solid containing the mixed powder 70 which consists of the silicon carbide particle 70 with a mean particle diameter of 10-100 micrometers - 95 mass %, and five to metal silicon particle 30 with a mean particle diameter of 1-50 micrometers mass % - 98 mass %, and the pore formation agent 2 - 30 mass % is used.

[0011] Although both the organic substance and an inorganic substance will be suitably used if decomposition etc. is carried out, it disperses as a pore formation agent at the time of heat treatment and pore is formed, it is desirable in their being a ceramic particle and the organic macromolecule particle of pyrolysis nature. Since it is served as work like sintering acid that a pore formation agent is a ceramic particle, it is desirable, and it is desirable in order not to spoil the property of the nature porous body of silicon carbide that it decomposes that it is the organic macromolecule particle of pyrolysis nature in a heat treatment process, and disperses on the other hand, and the residue may not be left behind in a sintered compact.

[0012] As a ceramic particle used for such a pore formation agent, oxide ceramics, nitride ceramics, carbide ceramics, the boride ceramics, etc. are mentioned. Since there is effectiveness like sintering acid to the nitriding cay elementary particle generated by nitriding especially, oxide ceramics are desirable, and since pore formation can be carried out in a small addition as it is the oxide-ceramics empty capsid (henceforth an empty capsid) which has especially a hollow configuration, it is still more desirable.

[0013] As an empty capsid, pore is formed at the time of heat treatment, and if the work like sintering acid is carried out to the nitriding cay elementary particle moreover generated in a heat treatment process, all will be used suitably. When the oxide of one or more sorts of metals chosen from the group which consists of aluminum, Si, calcium, Sr, Y, Yb, Ba, and Mg is used as a principal component, since the effectiveness like sintering acid is high, an empty capsid is desirable. As long as an empty capsid is hollow, the substantia compacta is sufficient as the part equivalent to an envelope, and porosity is sufficient as it. Moreover, although it is desirable since an empty capsid is it easy to come to hand that an appearance is a spherical particle, particles other than a spherical particle should just also be hollow.

[0014] The porosity of the porous body obtained as the mean particle diameter of an empty capsid is 30-100 micrometers is large, and since reinforcement is moreover also secured, it is desirable. A pore diameter turns it small up that the mean particle diameter of an empty capsid is less than 30 micrometers too much, and the contribution to pore formation falls. On the other hand, if mean particle diameter exceeds 100 micrometers, a pore diameter becomes large too much, and since the reinforcement of the porous body obtained is inadequate, it is not desirable.

[0015] Moreover, as an organic giant-molecule particle used as a pore grant agent, there are particles, such as polyvinyl alcohol, acrylic resin, vinyl acetate resin, and a cellulose. If the organic macromolecule particle added as a pore formation agent in the temperature up remains as carbon, without fully carrying out a pyrolysis in the temperature up phase of heat treatment, it will react with a metal silicon particle in a subsequent heat treatment process, not silicon nitride but silicon carbide will be generated, and it is not desirable in respect of improvement in thermal shock resistance. In that respect, since there are few amounts which will be easy to pyrolyze if an acrylic resin particle is made into a pore formation agent, and remain as carbon, it is desirable.

[0016] As a content of a pore formation agent, it is two to 30 in Plastic solid mass %. Under 2 mass % of the rate of pore is not enough as a content as a porous body, and on the other hand, if a content exceeds 30 mass %, although the porosity of a porous body will become large, sufficient reinforcement is not obtained. Since both the reinforcement of a porous body and porosity are highly made as the content of a pore formation agent is five to 25 in Plastic solid mass %, it is desirable.

[0017] Furthermore, especially since a strong fall can be controlled even if the pore formed as a pore formation agent is a globular form also becomes spherical and makes porosity high, it is desirable.

[0018] Moreover, it is suitable in the mean particle diameter of a pore formation agent being 5-100

micrometers. If the average pore diameter of the nature porous body of silicon carbide obtained after heat treatment as the mean particle diameter of a pore formation agent is less than 5 micrometers is set to 5 micrometers or less and it exceeds 100 micrometers on the other hand preferably, the average pore diameter of the nature porous body of silicon carbide obtained after heat treatment is set to 40 micrometers or more, and is not desirable as filters, such as dust removing.

[0019] The mean particle diameter of the metal silicon particle used for this manufacturing method is 1-50 micrometers. The amount which adsorbs oxygen and the moisture of the open air during Plastic solid creation etc. as the mean particle diameter of a metal silicon particle is less than 1 micrometer increases, and the amount of the silicon dioxide which oxidizes before a metal silicon particle is nitrided, when sintering cannot advance easily and also it heat-treats, and is generated becomes large too much. Moreover, if the mean particle diameter of a metal silicon particle exceeds 50 micrometers, the metal silicon particle which is not nitrided inside a sintered compact after heat treatment will remain, and the property as a final porous body will fall. In addition, as purity of a metal silicon particle, it is suitably chosen according to the purpose and an application.

[0020] In this manufacturing method, the usual ceramic fabricating methods, such as press forming, extrusion molding, and casting, are suitably adopted as an approach of creating the Plastic solid containing a pore formation agent and a metal silicon particle. In addition, on the occasion of shaping, an organic binder may be added apart from a pore formation agent. As such an organic binder, the organic substance, such as polyvinyl alcohol or its conversion object, starch or its conversion object, carboxyl methyl cellulose, hydroxyl methyl cellulose, a polyvinyl pyrrolidone, acrylic resin or an acrylic copolymer, vinyl acetate resin, or a vinyl acetate system copolymer, can be used. It is desirable when it is 1 - 10 mass section to said mixed powder 100 mass section as an addition of such an organic binder. In addition, a pore formation agent may serve as work of the binder of a Plastic solid.

[0021] As conditions which heat-treat said Plastic solid, it is desirable to hold at 1100-1800 degrees C under nitrogen-gas-atmosphere mind for 2 to 24 hours. In order that nitriding of a metal silicon particle may not progress that a temperature requirement is less than 1100 degrees C, since the nitriding cay elementary particle generated when it exceeded 1800 degrees C decomposes, it is not desirable preferably. Since association of the grain children whose temperature holding time is less than 2 hours does not fully advance, if it exceeds 24 hours on the other hand, it becomes [especially] easy to decompose silicon nitride at an elevated temperature and is not desirable preferably.

[0022] Although the programming rate at the time of heat treatment is suitably chosen by the magnitude of a Plastic solid, the configuration, etc., it is desirable in respect of the rate of nitriding, and a pore diameter in it being 50-600 degrees C/h. Although nitrogen-gas-atmosphere mind means the ambient atmosphere which does not contain oxygen only including nitrogen substantially here, other inert gas may be included. A nitrogen partial pressure has 50 or more desirable kPas.

[0023] The porosity of the nature porous body of silicon carbide (it only abbreviates to the nature porous body of this silicon carbide hereafter) obtained by this manufacturing method is suitable in it being 30 - 80%. When using as a filter that porosity is less than 30%, since pressure loss becomes large, it is not desirable as a porous body. Moreover, since reinforcement will become low if porosity exceeds 80%, it is not desirable as a porous body.

[0024] The average pore diameter of the nature porous body of this silicon carbide is desirable in it being 5-20 micrometers. It becomes [the pressure loss at the time of porous body use] large that an average pore diameter is less than 5 micrometers and is not desirable. Since it will be hard coming to carry out prehension removal of an exhaust air particle like a diesel particulate if an average pore diameter exceeds 20 micrometers, it is not desirable.

[0025] Since the organization of the nature porous body of this silicon carbide has the fine structure which combined the silicon carbide particle by silicon nitride and the metal silicon particle, it has the description which is excellent in thermal shock resistance.

[0026]

[Example] An example (Example 1, Example 4, Example 5) and the example of a comparison (Example 2, Example 3, Example 6) are shown below.

[0027] [Example 1] In the mixed powder 75 mass section of with a mean particle diameter of 50

micrometers silicon carbide particle 80 mass % and with a mean particle diameter of 10 micrometers metal silicon particle 20 mass %, 25 mass sections addition of the spherical particle of an acrylic resin system with a mean particle diameter of 20 micrometers was carried out, and ethanol was further added as a dispersion medium, and by the ball mill method, wet blending was carried out for 30 minutes, and it dried at the end. 40mmx60mm press metal mold was filled up with the obtained powder for Plastic solids, and 1 shaft pressing was performed by moulding pressure 20MPa. After shaping, in an electric furnace, and under nitrogen-gas-atmosphere mind, the temperature up was carried out by h in 400 degrees C /to room temperature -1000 degree C, and the temperature up was carried out by h in 60 degrees C /to 1500 degrees C, and at 1500 degrees C, it held for 10 hours, and heat-treated, and the porous body was obtained.

[0028] [Example 2] In Example 1, in the vacuum, heat treatment conditions carried out the temperature up by h in 400 degrees C /to room temperature -1000 degree C, carried out the temperature up by h in 300 degrees C /to 1350 degrees C, and obtained the porous body like Example 1 except holding at 1350 degrees C for 5 hours, and heat-treating.

[0029] [Example 3] In Example 1, the porous body was obtained like Example 1 except carrying out the temperature up of the heat treatment conditions by h in 400 degrees C /to room temperature -1000 degree C, they carrying out a temperature up by h in 300 degrees C /to 1000-1300 degrees C in an argon, holding them at 1300 degrees C for 5 hours, and heat-treating using the lithium aluminium silicate whose mean particle diameter is 10 micrometers instead of metal silicon.

[0030] [Example 4] The porous body was obtained like Example 1 except heat treatment conditions carrying out a temperature up by h in 400 degrees C /to room temperature -1000 degree C in nitrogen-gas-atmosphere mind, and carrying out a temperature up by h in 400 degrees C /to 1400 degrees C, carrying out time amount maintenance and heat-treating at 1400 degrees C, in Example 1.

[0031] [Example 5] In the mixed powder 85 mass section which consists of with a mean particle diameter of 75 micrometers silicon carbide particle 70 mass % and metal silicon particle 30 with a mean particle diameter of 10 micrometers mass %, the ceramic hollow spherical particle 15 mass section of an alumina silica system with a mean particle diameter of 40 micrometers was added, and ethanol was further added as a dispersion medium, and by the ball mill method, wet blending was carried out for 30 minutes, and it dried at the end.

[0032] 40mmx60mm press metal mold was filled up with the obtained powder for Plastic solids, and 1 shaft pressing was performed by moulding pressure 20MPa. After shaping, in an electric furnace, and under nitrogen-gas-atmosphere mind, the temperature up was carried out by h in 400 degrees C /to room temperature -1000 degree C, and the temperature up was carried out by h in 60 degrees C /to 1700 degrees C, and at 1700 degrees C, it held for 5 hours, and heat-treated, and the porous body was obtained.

[0033] [Example 6] The porous body was obtained like Example 1 except not using a metal silicon particle in Example 1.

[0034] The [evaluation approach] Porosity, an average pore diameter, coefficient of thermal expansion, a crystal phase, room temperature flexural strength, elevated-temperature flexural strength, acid resistance, and thermal shock resistance were measured and evaluated about each porous body.

Porosity (%): Measure by the Archimedes method.

Average pore diameter d (micrometer): Measure by the mercury porosimeter (the Yuasa Ionics make, trade name: AUTOSCAN-33).

Coefficient of thermal expansion α ($\times 10^{-6}/\text{degree C}$): Measure in room temperature -1000 degree C using a coefficients-of-linear-thermal-expansion measuring device (the Rigaku make, a trade name: TAS100).

Crystal phase: Identify according to an X diffraction. SC, SN, S, and LAS show the crystal phase of silicon carbide, silicon nitride, metal silicon, and lithium aluminosilicate, respectively.

Reinforcement sigma (MPa): From a sample, cut down the test piece for bend test of 4mmx3mmx40mm size, and measure three-point flexural strength (span 30mm) at a room temperature. The load impression rate was considered as a part for 0.5mm/. (%): The sample was immersed in the one-mol % sulfuric-acid water solution at 80 degree C for 50 hours, the three-point

flexural strength before and behind immersion was measured, respectively, and the decreasing rate on the strength from the flexural strength of the sample before immersion was computed and evaluated. [Corrosion-resistant] Corrosion resistance is so good that a decreasing rate on the strength is low. Thermal-shock-resistance ΔT : Iced water (about 3 degrees C) was made to throw in and quench the test piece held to the elevated temperature, the flexural strength of the test piece after quenching was measured, and the temperature gradient of the retention temperature when falling from the value of the flexural strength of the test piece before the value of flexural strength quenching and iced water was evaluated as a heat-resistant impact temperature gradient. The temperature gradient was evaluated at intervals of 50 degrees C. In addition, the test piece size of flexural strength and a test method apply to the above-mentioned measurement on the strength. An evaluation result is shown in Table 1.

[0035]

[Table 1]

	例 1	例 2	例 3	例 4	例 5	例 6
気孔率	3 5	4 0	3 0	3 7	4 0	5 0
d	1 5	1 7	1 6	1 2	1 5	2 0
結晶相	SC、SN	SC、S	SC、LAS	SC、SN、S	SC、SN	SC
α	3. 6	4. 1	3. 0	3. 8	3. 3	4. 6
σ	4 2	3 0	3 1	3 3	5 3	5
ΔT	5 0 0	3 0 0	4 0 0	4 0 0	5 0 0	3 0 0
耐食性	1 5	4 0	5 0	3 0	1 0	1 0

[0036] Compared with the nature porous body of silicon carbide which does not contain silicon nitride as it is a nature porous body of silicon carbide containing silicon nitride, it turns out that thermal shock resistance and corrosion resistance are improving.

[0037]

[Effect of the Invention] Compared with the carbonization siliceous porous body which does not contain the conventional nitriding cay elementary particle, the nature porous body of this silicon carbide containing the nitriding cay elementary particle which nitrided the metal silicon particle has the property excellent in thermal shock resistance, thermal resistance, corrosion resistance, chemical resistance, reinforcement, etc.

[0038] Therefore, it is suitable as a filter which deals with the intense gas of a temperature change, and the engine performance which was excellent especially as a particulate filter is shown.

[Translation done.]